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SYNTHESIS AND RESEARCH OF THE CHABAZITE-TYPE ZEOLITE ON THE BASIS OF NATURAL MINERAL OF NAKHCHIVAN

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Abstract

The optimal synthesis conditions for the practically important chabazite zeolite have been predicted based on the hydrothermal modification of the natural mineral of Nakhchivan of the Kyukyuchayfield.The starting component and hydrothermal reaction products have been identifiedby X-ray diffraction, thermogravimetric analysis and scanning electron microscope.The practically important chabazite zeolite has been identified by X-ray diffraction. The optimal conditions for its synthesis with a 100% degree of crystallization have been predicted. It has been established that the area of existence of chabazite is wide and the optimal conditions for its hydrothermal synthesis have been a temperature of 230°C, a concentration of a thermal solution of 15–20% $Ca(OH)_2$, of a mineralizer $CaCl_2$ of 10–15 % and a processing time of 100 hours. The obtained zeolite of chabazite was found to be stable up to 950°Cand dehydrated chabazite was completely rehydrated within 72 hours, which once again proves its zeolitic character. The data allow to predetermine the synthesis conditions of a practically important chabazite-type zeolite.

Keywords: Nakhchivan mineral; zeolite; chabazite; natural mineral; hydrothermal synthesis; optimal condition.

СИНТЕЗ І ДОСЛІДЖЕННЯ ЦЕОЛІТА ТИПУ ХАБАЗИТУ НА ОСНОВІ ПРИРОДНОГО МІНЕРАЛЬНОГО НАХЧІВАНА

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Анотація

Спрогнозовані оптимальні умови синтезу практично значущого цеоліту шабазиту на основі гідротермічної модифікації природного мінералу Нахічіван Кюкючай родовища. Вихідні компоненти та продукти гідротермальної реакції були визначені за допомогою рентгенівської дифракції, термогравіметричних методів аналізу та методу скануючої електронної мікроскопії. Практично важливий цеоліт шабазит був визначений рентгенографічно. Визначені оптимальні умови його синтезу зі 100%-ним ступенем кристалізації. Встановлена широка область існування шабазиту, а оптимальними умовами його гідротермічного синтезу стали: температура 230 °C, концентрація термального розчину 15–20 % $Ca(OH)_2$, мінералізатора $CaCl_2$ 10–15% та час обробки 100 годин. Встановлено, що отриманий цеоліт шабазит стійкий до 950 °C, а зневоднений шабазит повністю регідратується протягом 72 годин, що ще раз підтверджує його цеолітичний характер. Отримані дані дозволяють визначити умови синтезу практично важливого цеоліту типу шабазиту.

Ключові слова: Нахічівський мінерал; цеоліт; шабазит; природний мінерал; гідротермальний синтез; оптимальні умови.

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СИНТЕЗ И ИССЛЕДОВАНИЕ ЦЕОЛИТА ТИПА ШАБАЗИТА НА ОСНОВЕ ПРИРОДНОГО МИНЕРАЛА НАХЧЫВАНА

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Аннотация

Спрогнозированы оптимальные условия синтеза практически значимого цеолита типа шабазита на основе гидротермальной модификации природного минерала Нахчывана Кюкючайского месторождения. Исходный компонент и продукты гидротермальной реакции были идентифицированы рентгенографическим, термогравиметрическим методами анализа и методом сканирующей электронной микроскопией. Цеолит шабазит был исследован методом рентгеновской дифракции, и были установлены оптимальные условия его синтеза со 100%-ной степенью кристалличности. Установлена широкая область существования шабазита, а оптимальными условиями его гидротермального синтеза оказались: температура 230 °C, концентрация термального раствора $Ca(OH)_2$ 15–20 %, минерализатора $CaCl_2$ 10–15 % и время обработки 100 часов. Было установлено, что полученный цеолит шабазит стабилен до 950 °C, а дегидратированный шабазит полностью регидратируется в течение 72 часов, что еще раз подтверждает его цеолитный характер. Полученные данные позволяют заранее предопределить условия синтеза практически важного цеолита типа шабазита.

Ключевые слова: минерал Нахчывана; цеолит; шабазит; природный минерал; гидротермальный синтез; оптимальные условия.

Introduction

Research activity in the field of the synthesis of zeolites based on natural minerals, as well as the study of the Nakhchivan zeolite is a promising and urgent task of our time. The fact is that research activity on the basis of natural minerals reduces the country's dependence on foreign raw materials, contributes to the rational use of natural resources of the Nakhchivan Autonomous Republic (NAR) and its use in various areas of the national economy.

It is known that zeolites, synthetic or natural, have a wide range of application – starting with a catalyst [1–7] and ending with an adsorbent [8–17].

The need to study the hydrothermal recrystallization of zeolite-containing rocks is associated with the possibility of using them to obtain zeolites of other structural types with improved properties.

The development of the scientific background of the synthesis and fields of application of zeolites, as well as the implementation of crystallization based on local mineral raw materials is currently one of the important areas of basic research.

The use of local mineral raw materials (low-cost materials) in the synthesis of zeolites becomes an area of great interest and plays an active role in advancing technological advances related to scientific research and production technologies of zeolite materials in optimized experimental conditions.

Numerous studies have been conducted on the synthesis of zeolites based on zeolite-bearing rocks of various countries.

In [18], the conversion of natural zeolite into Na-A zeolite by the two-step method has been carried out. Silicon dioxide used as a starting component was obtained from zeolite tuff and sodium aluminate from chemical reagents. The process was carried out at 90–100°C in a time interval of 0.5-4 hours, and as a result Na-A was obtained with maximum crystallinity. Despite the moderate synthesis conditions, it took a lot of time and material costs to obtain the initial components.

In the work by Tatlier and Atalay-Oral, [19] zeolite A was obtained from natural clinoptilolite under more severe conditions.

In [20], hydrothermal synthesis of ZSM-5 zeolite was carried out from natural zeolite of Bayat-Klaten at 250 °C, in the presence of tetrapropylammonium hydroxide and 40 % silica suspension in water. As can be seen, numerous chemicals were used for hydrothermal synthesis.

Our proposed method can provide more cost-efficient mass-scale production of synthetic zeolites based on cheaper natural resources.

A series of zeolites was synthesized in hydrothermal conditions,phase-wise both in its pure formand in the form of associations, on the basis of the natural zeolite of the Kyukyuchai deposit of the Nakhchivan AR [21–23]. It has been established that the use of local natural raw materials from the Kyukyuchai deposit contributes to the process under moderate

conditions, obtaining purephase-crystalline products.

In [24–26] chabazite was obtained on the basis of organic structure-directing agents. But synthesis based on them is expensive and toxic.

Considering the above, the purpose of this research work is to study the hydrothermal modification of the natural sample of Nakhchivan with the production of zeolite such as chabazite and the establishment of optimal conditions for its synthesis using local natural raw materials from the Kyukyuchai deposit of the Nakhchivan AR. Usage of local natural resources reduces dependency on the foreign raw stock and it leads to the reasonable use of natural resources. Furthermore, it can bring certain benefits to the national economy.

Compared with the published data [27; 28] the chabazite synthesized by us is characterized by maximum crystallinity (100 %).

We have been the first to carryout a chemical modification of the natural mineral material of Nakhchivan, to synthesize of chabazite based on it, and we have also determined the optimal synthesis conditions.

Results and discussions

Zeolitic tuffs of Nakhchivan have been used as a source of samples, 78.5 % of which is the major mineral – mordenite (1), 19.5% is quartz (2) and 2.00 % is anortithe (3).

$$Ca_2Na_2K_{2.8}Al_{8.8}Si_{39.2}O_{96}\cdot 34H_2O \quad (1)$$

$$SiO_2 \quad (2)$$

$$Ca_{0.86}Na_{0.14}Al_{1.94}Si_{2.06}O_{8.01} \quad (3)$$

The chemical composition of the natural zeolite of Nakhchivan is given in the Table 1.

Table 1

The percentage of oxides and elements in the composition of the natural sample of zeolite

Element	Weight (%)	Atomic (%)	Amount of oxides (%)	Formula
Na	0.42	0.37	0.56	Na_2O
Mg	0.38	0.32	0.63	MgO
Al	4.49	3.38	8.48	Al_2O_3
Si	39.90	29.08	85.93	SiO_2
K	0.75	0.39	0.90	K_2O
Ca	1.14	0.58	1.59	CaO
Fe	0.87	0.32	1.12	FeO
Ti	0.63	0.25	0.78	TiO_2
O	51.42	65.32		
Total	100.00			

The hydrothermal synthesis experiments of the chabazite-type zeolite were conducted in a time interval of 50–100 hours, at the temperature of 200–300 °C. The concentrations of $Ca(OH)_2$ thermal solution and mineralizer $CaCl_2$ was studied in the range of 5–30 %.

According to experimental data, the optimal temperature for the synthesis of the chabazite is 230°C, concentration of $Ca(OH)_2$thermal solution is 15–20 %, concentration of mineralizer $CaCl_2$is 10–15 % and the crystallization process takes 100 hours. Under the presented optimal conditions, a pure phase-stable chabazite has been obtained.

As can be seen from Table 2, the change in temperature and processing time has a significant effect on the crystallinity degree of synthesized chabazite.The crystallinity of the samples was calculated from the relative peak intensities. On standards of the American Society for Testing and Materials, the percentage of crystallinity is determined by the formula [29]:

Crystallinity (%) = Sample peak intensity/Standart peak intensity 100%

Table 2

The degree of crystallinity of synthesized chabazite at various temperatures and processing time

		Degree of crystallinity, %
Temperature, ^{0}C	200	70
	230	100
	250	80
	300	40
	320	-
Time of processing, hour	50	40
	60	50
	70	60
	90	80
	100	100

The study of the process began at a temperature of 200 ^{0}C, at which the degree of crystallinity is 70 %, i.e., the initial mass does not completely crystallize into the reaction product. In addition to chabazite, quartz and anorthite are present in the reaction products. At 230 ^{0}C, the entire initial mass recrystallizes into chabazite. A further increase in temperature (250 and 300 ^{0}C) leads to a decrease in the degree of crystallinity of chabazite, and in addition to it, albite crystallizes in the composition of the product. And at 320 ^{0}C, the synthesis products are albite and quartz.

Changes in the degree of crystallinity of synthesized chabazite are also observed with a change in processing time. The crystallization process has been investigated in a time interval of 50–100 hours. For 50 hours, the degree of crystallinity of chabazite is 40 % and besides it, anorthite and quartz are present in the reaction

products. A further increase in the processing time (60, 70, 90 hours) leads to an increase in the degree of crystallinity of chabazite, but in addition to the main product, anorthite and quartz are present in the reaction products. For 100 hours of treatment, the degree of crystallinity of chabazite reaches 100 %.

The diffraction patterns of natural mineral raw materials of Nakhchivan and the products of hydrothermal crystallization at various temperatures are presented in Figure 1 and Figures 2, and the tabulated data of X-ray diffraction analysis of chabazite is given in Table 3.

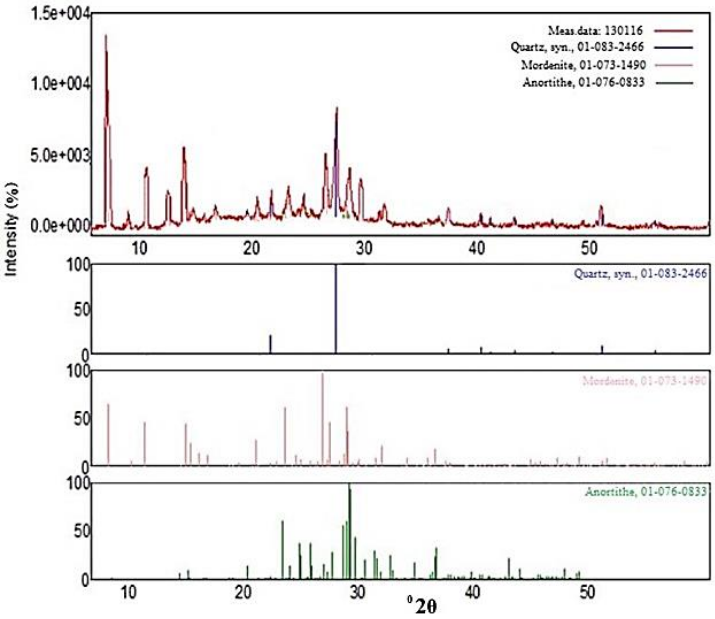

Fig. 1. XRD patterns of Nakhchivan natural zeolite

Table 3

X-ray data of synthesized chabazite

Chabazite			
d_{exp}, Å	I_{rel}	hkl	d_{calc}, Å
9.44	100	100	9.45
6.68	20	101	6.68
5.46	25	111	5.46
4.24	50	201	4.23
3.89	40	211	3.86
3.36	10	202	3.34
3.14	10	300	3.15
3.05	10	301	3.00
2.94	70	311	2.85
2.62	15	320	2.62
2.52	20	312	2.52
2.32	10	322	2.29
2.23	10	303	2.23
2.17	10	402	2.11
2.10	15	412	2.06
2.07	10	323	2.01
1.96	10	422	1.93
1.88	10	500	1.89
1.87	10	501	1.86

When comparing X-ray diffraction experimental data with literature data [30], it was established that the sample under study is a zeolite – mordenite and the synthesized product of chabazite (Table 3). The interference maxima characteristic of the mordenite phase correspond to the values of the Bragg angle 2θ = 6.5, 9.8, 13.5, 14, 19.5, 22, 25.5, 26, 27, 28, etc. The relative intensity and interplanar distances obtained experimentally correspond to the literature data (within the experimental error), which indicates that mordenite is the main phase of the sample. The interplanar distances (d) and the intensities of the diffraction lines (I) equal to d=3.34 Å (100),

2.45 Å (30), 2.28 Å (201) and 2.12 Å (20) indicate that that the sample contains silicon dioxide, i.e. *α*-quartz. According to the diffractogram anortithe (4.30 Å, 3.60 Å, 3.40 Å, 3.19 Å) is also present in the sample composition in small quantitie.

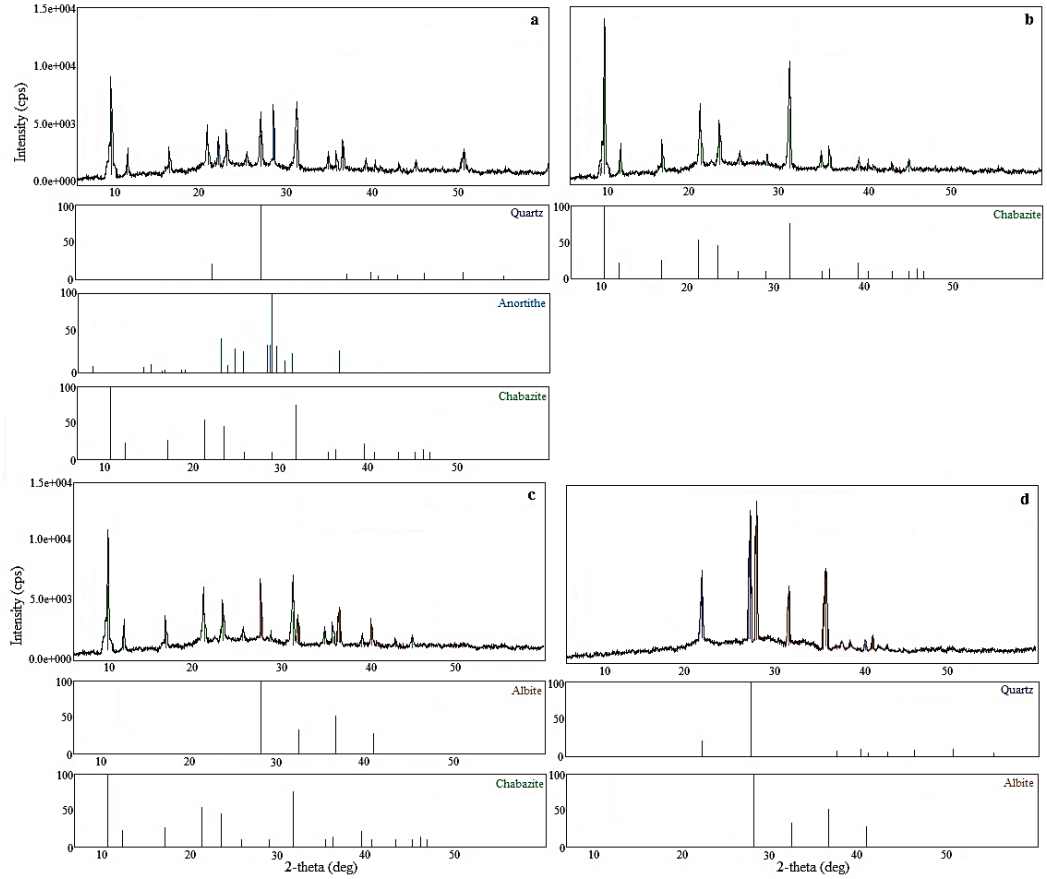

Fig. 2. XRD patterns of hydrothermal crystallization products at 200° C (a), 230 °C (b), 250 and 300 °C (c), 320 °C (d)

The obtained hydrothermal modification of natural mineral raw of Nakhchivan chabazite crystallizes in the cubic crystal system with the unit cell parameter a = 9.459 Å, which agrees well with the reference data [31].

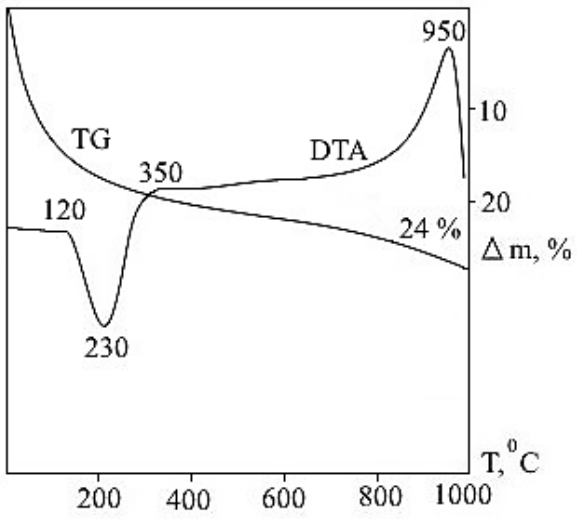

Fig. 3. DTA and TG curves of chabazite with 100% degree of crystallinity

The area of dehydration, water content and thermal stability of chabazite are determined by the method of thermogravimetricanalysis. The DTA and TG curves are presented in Fig. 3.

DTA curves are characterized by one endothermic and one exothermic effects.

The first endothermic effect refers to the dehydration of the sample. The hydration shell of cations with a maximum of 230 ^{0}C is subjected to dehydration that occurs with a loss of the TG curve of 24 %.

The dehydration and rehydration properties of the obtained chabazite were studied. Since we received chabazite thermal stability, the process of dehydration has been reversible, characteristic for zeolite. The sample dehydrated at 120–350 ^{0}C is completely rehydrated within 72 hours, i.e. dehydration is reversible.

Ifa change in the structure of the zeolite is observed in the process of dehydration, then the DTA curve becomes more complex, that is, multiple excesses appear. Like the wine from Figure 3, the DTA curve is smooth, that is, there is no structural change during dehydration.

The second endothermic effect, with a maximum of 950 ^{0}C, observed at high temperature, according to X-ray analysis,

corresponds to the destruction of the crystal structure of chabazite with the formation of hydrosodalite. The diffractogram of hydrosodalite is presented in Fig. 4.

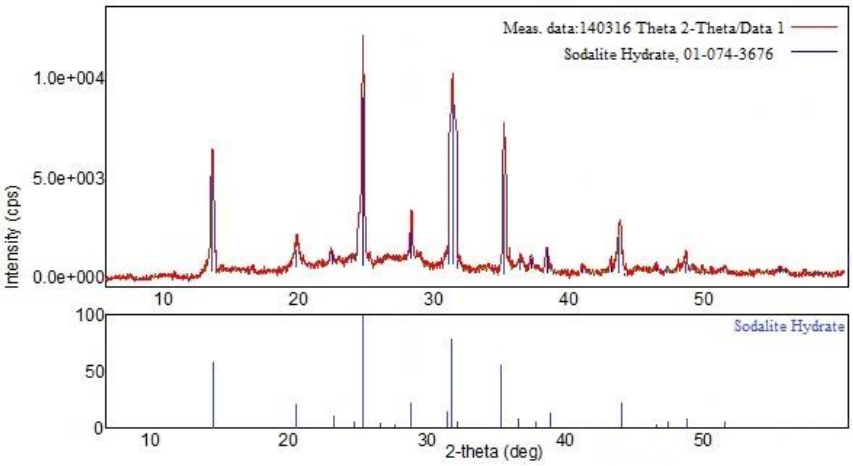

Fig. 4. XRD patterns of hydrosodalite

Hydrosodalite crystallizes in the cubic crystal system with the unit cell parameter a = 8.85 Å, which agrees well with the reference data [31].

Fig. 5 shows the micrographs of the synthesized products. As can be seen from figure 5 the individual phase of chabazite crystallizes in an indefinite form of nanoparticles.

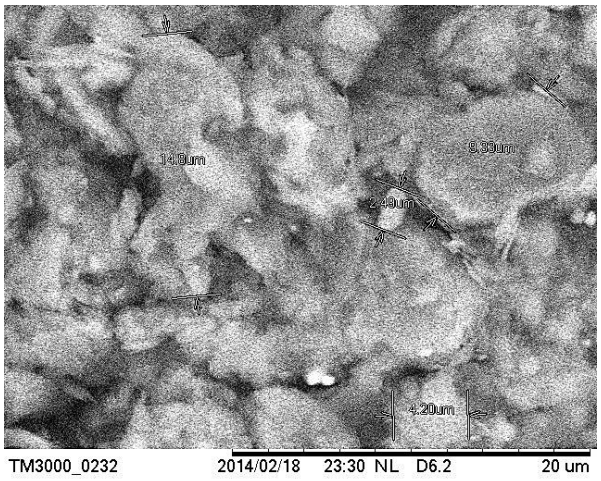

Fig. 5. Micrograph of chabazitewith 100% degree of crystallinity

Materials and methods

Instrumentation. The initial component and the reaction products were examined by X-ray, thermogravimetric analysis and scanning electron microscope.

XRD analysis. The X-ray diffraction measurements were performed using the X-ray analyzer 2D PHASER "Bruker" (Cu K_α radiation, 2θ = 5–50°), using of NaCl, SiO_2 (quartz) and pure zeolites in internal and external standards. Samples have been placed on a front mounted plastic sample holder. The measuring conditions have been as follows: step size of 0.15 s/step, nickel filter as incident beam, slit aperture of 0.3° and scan range from 0.5° to 10° 2θ.

Thermogravimetric analysis. The thermos-gravimetric analysis of the samples has been carried out on a "Q-Derivatograph 1500-D" of the Hungarian company MOM in the dynamic mode in the temperature range 20–1000 ^{0}C. Shooting mode: heating rate of 20°/min; paper speed of 2.5 mm/min; the sensitivity of DTA, DTG and TG is 500 mv; ceramic crucibles; the standard is Al_2O_3.

Scanning electron microscopic analysis. The scanning electron microscopic analysis of the starting materials and reaction products was carried out on a Hitachi 3000 TM high resolution microscope (magnification 30000 times). The low vacuum mode allows to examine samples without preliminary spraying. The sample is placed on a double-sided adhesive tape glued to a metal disk and vacuum to a pressure of 10^{-4} Pa, then the sample is viewed under a microscope and a micrograph is obtained.

Natural mineral. The natural sample has been obtained from the zeolite horizon in the north-west of the Kyukyuchai river where zeolite content varies in the range of 75–80 %. The sample has thoroughly been washed with distilled water and dried at the temperature of 100 °C for three days.

Chemicals. Calcium hydroxide and calcium chloride (flake, 99 % purity, Alfa Aesar GmbH & Co KG, Germany) have been used as received without further purification.

Working methods. The hydrothermal synthesis has been carried out in Morey type autoclaves madeof 45MNFT stainless steel with a volume of 18 cm^3, and with the filling coefficient of F = 0.8. The hydrothermal crystallization experiments

have been carried out on generating a temperature gradient ΔT = 0 and without stirring of the reaction mass. Solid–liquid ratio is 1:10. For each experiment, 2 g of natural zeolite has been used.After crystallization is completed, the final material is separated from the initial solution. It is washed with distilled water from excess alkali, and dried at 80 °C.

Conclusions

Thus, the hydrothermal modification of natural mineral raw materials of Nakhchivan was obtained initially and a practically important zeolite of chabazite type was synthesized. A hydrothermal modification was carried out in wide ranges of temperature, concentration of thermal solution and treatment time. It was found that the optimal conditions for the synthesis of phase-pure chabazite were temperature of 230 °C, concentration of thermal solution – 15–20 % $Ca(OH)_2$, concentration of mineralizer – 10–15 % $CaCl_2$ and treatment time – 100 hours. It was established that the resulting zeolite of chabazite was dehydrated in the temperature range of 120–350 °C, stayed stable up to 950 °C, and a further increase in temperature leads to the destruction of its structure and crystallization of hydrosodalite. It was shown that dehydrated chabazite is completely rehydrated within 72 hours, which once again proves its zeolite character. Based on the natural zeolite of Nakhchivan, a series of synthetic practically important zeolites can be synthesized (directed synthesis).

Bibliography

[1] Пат. 02311620 США, МПК[8] B01J29/88, B01D53/94. Iron-zeolite chabazite catalyst for use in NO_X reduction and method of making / Clifford M. N. (США); заявник та патентовласник Clifford M. N. (США), Ford Global Technologies. – № 14/183969; заявл. 19.02.14; опубл. 20.08.15. – 10 с.

[2] Пат. 0020204 США, МПК[8] B01J29/70, B01 J29/76, B01D53/56, B01J37/30, B01D50/00. Chabazite zeolite catalysts having low silica to alumna ratios / Bull I., Moini A., Rai M. (США); заявник та патентовласник Bull I. (США), Moini A. (США), Rai M. (США), BASF Catalysts LLC. – № 12/612,142; заявл. 04.11.09; опубл. 27.01.11. – 14 с.

[3] Christopher J. R. The Properties and Applications of Zeolites // Science Progress. – 2010. – Vol. 93, N 3. – P. 1–63.

[4] Jonghyun K. Facile Synthesis of KFI-type Zeolite and Its Application to Selective Catalytic Reduction of NO_x with NH_3 / K. Jonghyun, J. C. Sung, K. Do Heui // ACS Catal. – 2017. – Vol. 7, N 9. – P. 6070–6081.

[5] Rozanska X. A periodic density functional theory study of gallium-exchanged mordenite / X. Rozanska, M. Garcia-Sanchez, E. J. M. Hensen, R. A. Van Santen // Comptes Rendus Chimie, – 2005. – Vol. 8, N 3–4. – P. 509–520.

[6] Alkaline-acid treated zeolite L as catalyst in ethanol dehydration process / A. T. Karolina, T. Justyna, F. Urszula [et al.] // Microporous and Mesoporous Materials. – 2017. – Vol. 241. – P. 132–144.

[7] Effect of zeolite particle size and internal grain boundaries on Pt/Beta catalyzed isomerization of n-pentane / Y. Guanghua, S. Yuanyuan, G. Zhougyuan [et al.] // Journal of Catalysis. – 2018. – Vol. 360. – P. 152–159.

[8] Yulius D. N. Hydrothermal Transformation of Natural Zeolite from Ende-NTT and Its Application as Adsorbent of Cationic Dye / D. N. Yulius, S. Sri, A. Zaenal // Indones. J. Chem. – 2016. – Vol. 16, N 2. – P. 138–143.

[9] Nobuyuki T. Ion-exchange properties of zeolite/glass hybrid materials / T. Nobuyuki, Y. Kohei, F. Takuya // J. of the Ceramic Society of Japan. – 2017. – Vol. 125, N 5. – P. 427–429.

[10] Min J. G. Zeolites ZSM-25 and PST-20: Selective Carbon Dioxide Adsorbents at High Pressures / J. G. Min, B. H. Suk, K. K. Christian // The Journal of Physical Chemistry C. – 2017. – Vol. 121, N 6. – P. 3404–3409.

[11] Nazarenko O. B. Badinsk zeolite application for ground water treatment / O. B. Nazarenko, F. Z. Rayisa, S. V. Anastasya // 7th Intern. For. on Strategic tech., Tomsk. – 2012. – P. 357.

[12] Mokarami S.Gh. Zeolite application to sea water for ammonia absorbtion and its effects on growth and survival of Penaeus indicus / S. Gh. Mokarami, H. Emadi // Iranian Scientific Fisheries Journal. – 2007. – Vol. 16, N 2. – P. 127–136.

[13] Karapinar N. Application of natural zeolite for phosphorus and ammonium removal from aqueous solutions // J. Hazard. Mater. – 2009. – Vol. 170, N 2–3. – P. 1186–1191.

[14] Bacakova L. Applications of zeolites in biotechnology and medicine – a review / L. Bacakova, M. Vandrovcova, I. Kopova, I. Jirka // Biomaterials Science. – 2018. – Vol. 6, N 5. – P. 974–989.

[15] Use of chabazite, a naturally abundant zeolite, for the investigation of the adsorption kinetics and mechanism of methylene blue dye / H. Aysan, S. Edebali, C. Ozdemir [et al.] // Microporous and Mesoporous Materials. – 2016. – Vol. 235. – P. 78–86.

[16] Sepaskhah A. R. Effects of zeolite application on nitrate and ammonium retention of a loamy soil under saturated conditions / A. R. Sepaskhah, F. Yousefi // Australian Journal of Soil Research. – 2007. – Vol. 45, N 5. – P. 368–373.

[17] Ibrahim K. Use of natural chabazite–phillipsite tuff in wastewater treatment from electroplating factories in Jordan / K. Ibrahim, N. Ed-Deen, H. Khoury // Environmental Geology. – 2002. – Vol. 41, N 5. – P. 547–551.

[18] Sariman. Synthesis of Na-A zeolite from natural zeolites // Indonesian Mining Journal. – 2005. – Vol. 8, N 1. – P. 37–51.

[19] Tatlier M. Crystallization of Zeolite A Coatings from Natural Zeolite / M. Tatlier, C. Atalay-Oral // Materials Research. – 2016. – Vol. 19, N 6. – P. 1469–1477.

[20] Synthesis and Characterization of ZSM-5 Zeolite from Dealuminated and Fragmentated Bayat-Klaten Natural Zeolite / Y. K. Krisnandi, I. Mahmuda, D. U. C. Rahayu, R. Sihombing // The 6th International Conference of the Indonesian Chemical Society, Indonesia. – 2018. – P. 250–254.

[21] Мамедова Г. А. Модификация природного цеолита Нахчывана в щелочной среде // Вестник Московского Университета. – 2019. – Т. 74, N 1. – С. 46–53.
[22] Мамедова Г. А. Гидротермальный синтез цеолита ZSM-10 // Вестник Московского Государственного Технического Университета им. Н.Э. Баумана. – 2018. – Т. 80, N 5. – С. 139–145.
[23] Мамедова Г. А. Химическая модификация природного минерала Нахчывана / Г. А. Мамедова, Ф. М. Новрузова // Перспективные материалы. – 2018. – N 6. – С. 54–61.
[24] Nuria M. G. High yield synthesis of high-silica chabazite by combining the role of zeolite precursors and tetraethylammonium: SCR of NO_x / M. G. Nuria, M. M. Manuel, C. C. Avelino // Chem. Commun. – 2015. – Vol. 51. – P. 9965–9968.
[25] Пат. 3233734 (A1) Европа, МПК7 C01B39/02. Synthesis of zeolite with the cha crystal structure, synthesis process and use thereof for catalytic applications / Avelino C. C., Manuel M. M., Nuria M. G. (Испания); заявник та патентовласник Universidad Politecnica de Valencia (Испания). – № EP 3233734; заявл. 11.12.15; опубл. 25.10.17. – 15 с.
[26] Single parameter synthesis of high silica CHA zeolites from fluoride media / E. A. Eilertsen, B. Arstad, S. Svelle, K. P. Lillerud // Micropor. Mesopor. Mat. – 2012. – Vol. 153. – P. 94–99.
[27] Eco-friendly synthesis of kaolin-based chabazite for CO_2 capture / C. Shuai, D. Tao, Z. Sulong [et al.] // Journal of the Ceramic Society of Japan. – 2019. – Vol. 127, N 9. – P. 606–611.
[28] Synthesis of nanocontainer chabazites from fly ash with a template-and fluoride-free process for cesium ion adsorption / T. Du, X. Fang, Y. C. Wei, J. Shang // Energ. Fuel. – 2017. – Vol. 31, N 4. – P. 4301–4307.
[29] Effect of Crystallization Time on the Synthesis of Zeolite Y from Elefun Kaolinite Clay / A. A. Ayoola, F. K. Hymore, J. O. Omodara [et al.] // International Journal of Applied Engineering Research. – 2017. – Vol. 12, N 21. – P. 10981–10988.
[30] Analysis of theoretical and experimental X-ray diffraction patterns for distinct mordenite frameworks / P. Sánchez-López, J. Antúnez-García, S. Fuentes-Moyado [et al.] // J. Mat. Sci. – 2019. – Vol. 54, N 10. – P. 7745–7757.
[31] Treacy M. M. Collection of simulated XRD powder patterns for zeolites // M. M. Treacy, J. B. Higgins. – New York, USA: Elsevier, 2001. – 586 p.

References

[1] Clifford, M. N. (2015). *US Patent No.0231620.* Washington, DC: U.S. Patent and Trademark Office.
[2] Bull, I., Moini, A., Rai, M. (2011). *US Patent No. 0020204.* Washington, DC: U.S. Patent and Trademark Office.
[3] Christopher, J.R. (2010). The Properties and Applications of Zeolites. *Science Progress*, *93*(3), 1–63. http://dx.doi.org/10.3184/003685010X12800828155007
[4] Jonghyun, K., Sung, J.C., Do Heui, K. (2017). Facile Synthesis of KFI-type Zeolite and Its Application to Selective Catalytic Reduction of NO_x with NH_3. *ACS Catal.*, *7*(9), 6070–6081. https://doi.org/10.1021/acscatal.7b00697
[5] Rozanska, X., Garcia-Sanchez, M., Hensen, E.J.M., Van Santen, R.A. (2005). A periodic density functional theory study of gallium-exchanged mordenite. *Comptes Rendus Chimie*, *8*(3–4), 509–520. http://dx.doi.org/10.1016/j.crci.2004.11.013
[6] Karolina, A.T., Justyna, T., Urszula, F., Agnieszka, S., Iwona, T., Kinga, G.M. (2017). Alkaline-acid treated zeolite L as catalyst in ethanol dehydration process. *Microporous and Mesoporous Materials*, 241, 132–144. https://doi.org/10.1016/j.micromeso.2016.12.035
[7] Guanghua, Y., Yuanyuan, S., Zhougyuan, G., Kake, Z., Honglai, L., Xinggui, Z., Coppens, M-O. (2018). Effect of zeolite particle size and internal grain boundaries on Pt/Beta catalyzed isomerization of n-pentane. *Journal of Catalysis*, 360, 152–159. https://doi.org/10.1016/j.jcat.2018.01.033
[8] Yulius, D. N., Sri, S., Zaenal, A. (2016). Hydrothermal Transformation of Natural Zeolite from Ende-NTT and Its Application as Adsorbent of Cationic Dye. *Indones. J. Chem.*,16(2),138–143. https://doi.org/10.22146/ijc.21156
[9] Nobuyuki, T., Kohei, Y., Takuya, F. (2017). Ion-exchange properties of zeolite/glass hybrid materials. *J. of the Ceramic Society of Japan*, 125(5), 427–429. http://dx.doi.org/10.2109/jcersj2.17028
[10] Min, J.G., Suk, B.H., Christian, K.K. (2017). Zeolites ZSM-25 and PST-20: Selective Carbon Dioxide Adsorbents at High Pressures. *The Journal of Physical Chemistry C*, *121*(6), 3404–3409. https://doi.org/10.1021/acs.jpcc.6b11582
[11] Nazarenko, O.B., Rayisa, F.Z., Anastasya, S.V. (2012). Badinsk zeolite application for ground water treatment. *7th Intern. For. on Strategic tech.,* Tomsk, 2012, 357.
[12] Mokarami, S.Gh., Emadi, H. (2007). Zeolite application to sea water for ammonia absorbtion and its effects on growth and survival of Penaeus indicus. *Iranian Scientific Fisheries Journal*, *16*(2), 127–136. http://aquaticcommons.org/id/eprint/23651
[13] Karapinar, N. (2009). Application of natural zeolite for phosphorus and ammonium removal from aqueous solutions. *J. Hazard. Mater., 170*(2–3), 1186–1191. https://doi.org/10.1016/j.jhazmat.2009.05.094
[14] Bacakova, L., Vandrovcova, M., Kopova, I., Jirka, I. (2018). Applications of zeolites in biotechnology and medicine – a review. *Biomaterials Science*, *6*(5), 974–989. http://doi.org/10.1039/C8BM00028j
[15] Aysan, H., Edebali, S., Ozdemir, C., Karakaya, M. C., Karakaya, N. (2016). Use of chabazite, a naturally abundant zeolite, for the investigation of the adsorption kinetics and mechanism of methylene blue dye. *Microporous and Mesoporous Materials*, 235, 78–86.https://doi.org/10.1016/j.micromeso.2016.08.007
[16] Sepaskhah, A.R., Yousefi, F. (2007). Effects of zeolite application on nitrate and ammonium retention of a loamy soil under saturated conditions. *Australian Journal of Soil Research*, *45*(5), 368–373. http://dx.doi.org/10.1071/SR06069
[17] Ibrahim, K., Ed-Deen, N., Khoury, H. (2002). Use of natural chabazite–phillipsite tuff in wastewater treatment from electroplating factories in Jordan. *Environmental Geology*, *41*(5), 547–551. http://dx.doi.org/10.1007/s002540100430
[18] Sariman (2005). Synthesis of Na-A zeolite from natural zeolites. *Indonesian Mining Journal*, 8(1), 37–51.
[19] Tatlier, M., Atalay-Oral, C. (2016). Crystallization of Zeolite A Coatings from Natural Zeolite. *Materials Research*, *19*(6), 1469–1477. http://dx.doi.org/10.1590/1980-5373-MR-2016-0564
[20] Krisnandi, Y.K., Mahmuda, I., Rahayu, D.U.C., Sihombing, R. (2018). Synthesis and Characterization

of ZSM-5 Zeolite from Dealuminated and Fragmentated Bayat-Klaten Natural Zeolite. *The 6th International Conference of the Indonesian Chemical Society*, Indonesia, 250–254.

[21] Mamedova, G. A. (2019). [Modification of a Nakhchivan natural zeolite in the alkaline environment]. *Mosc. Univ. Chem. Bull.*, *74*(1), 46–53 (in Russian). http://doi.org/10.3103/S0027131419010085

[22] Mamedova, G. A. (2018). [Hydrothermal synthesis of zeolite ZSM-10]. *Bulletin of the Moscow State Technical University. N.E. Bauman*, *80*(5),139–145 (in Russian). http://doi.org/10.18698/1812-3368-2018-5-125-133

[23] Mamedova, G. A., Novruzova, F. M. (2018). [Chemical modification of the natural mineral Nakhchivan]. *Perspective materials*, 6, 54–61 (in Russian). http://doi.org/10.30791/1028-978x-2018-6-54-61

[24] Nuria, M. G., Manuel, M. M., Avelino, C. C. (2015). High yield synthesis of high-silica chabazite by combining the role of zeolite precursors and tetraethylammonium: SCR of NO_x. Chem. Commun., 51, 9965–9968. https://doi.org/10.1039/C5CC02670A

[25] Avelino, C. C., Manuel, M. M., Nuria, M. G. (2017). European Patent No. EP3233734A1. European Patent Office.

[26] Eilertsen, E. A., Arstad, B., Svelle, S., Lillerud, K. P. (2012). Single parameter synthesis of high silica CHA zeolites from fluoride media. *Micropor. Mesopor. Mat.*, 153, 94–99. 10.1016/j.micromeso.2011.12.026

[27] Shuai, C., Tao, D., Sulong, Z., Xin, F., Yisong, W. (2019). Eco-friendly synthesis of kaolin-based chabazite for CO_2 capture. Journal of the Ceramic Society of Japan, *127*(9), 606–611. http://doi.org/10.2109/jcersj2.19056

[28] Du, T., Fang, X., Wei, Y. C., Shang, J. (2017). Synthesis of nanocontainer chabazites from fly ash with a template- and fluoride-free process for cesium ion adsorption. Energ. Fuel., *31*(4), 4301–4307. https://doi.org/10.1021/acs.energyfuels.6b03429

[29] Ayoola, A.A., Hymore, F.K., Omodara, J.O., Oyeniyi, A.E., Ojo, S.F.,Chisom U. (2017). Effect of Crystallization Time on the Synthesis of Zeolite Y from Elefun Kaolinite Clay. *International Journal of Applied Engineering Research*, *12*(21), 10981–10988.

[30] Sánchez-López, P., Antúnez-García, J., Fuentes-Moyado, S., Galván, D., Petranovskii, V. (2019). Analysis of theoretical and experimental X-ray diffraction patterns for distinct mordenite frameworks. *J. Mat. Sci.*, *54*(10), 7745–7757. http://doi.org/10.1007/s10853-019-03407-w

[31] Treacy, M. M., Higgins, J. B. (2001). *Collection of simulated XRD powder patterns for zeolites.* New York, USA: Elsevier.